Effect of Poly(styrene-*co*-maleic anhydride) Imidization on the Miscibility and Phase-Separation Temperatures of Poly(styrene-*co*-maleic anhydride)/Poly(vinyl methyl ether) and Poly(styrene-*co*-maleic anhydride)/Poly(methyl methacrylate) Blends

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ABSTRACT: The objective of this work was to study the miscibility and phase-separation temperatures of poly(styrene-*co*-maleic anhydride) (SMA)/poly(vinyl methyl ether) (PVME) and SMA/poly(methyl methacrylate) (PMMA) blends with differential scanning calorimetry and small-angle light scattering techniques. We focused on the effect of SMA partial imidization with aniline on the miscibility and phase-separation temperatures of these blends. The SMA imidization reaction led to a partially imidized styrene *N*-phenyl succinimide copolymer (SMI) with a degree of conversion of 49% and a decomposition temperature higher than that of SMA by about 20°C. We observed that both SMI/PVME and SMI/PMMA blends had lower critical solution temperature behavior. The imidization of SMA increased the phase-separation temperature of the SMA/PVME blend and decreased that of the SMA/PMMA blend. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 109: 3938–3943, 2008

Key words: blends; differential scanning calorimetry (DSC); miscibility; phase separation

INTRODUCTION

Because of their good heat resistance, copolymers of styrene and maleic anhydride (MA), that is, poly(styrene-*co*-maleic anhydride)s (SMAs), are widely used in commercial applications requiring good performance at elevated temperatures. Further improvement of the thermal stability of SMA can be realized by the conversion of the anhydride groups to the corresponding imide groups through a reaction with aliphatic and aromatic primary amines either in solution or in the melt (reactive extrusion) and through the direct polymerization of N-substituted or non-substituted maleimides.[1–3] The thermal properties depend on the degree of conversion of both the ring-opening and ring-closing reactions.[4] An increase in the conversion degree of the ring-opening reaction leads to an increase in the glass-transition temperature (T_g) of SMA because of the intermolecular hydrogen bonds between the carboxylic acid groups. However, an increase in the conversion degree of the ring-closing reaction leads to a decrease in T_g of SMA because of the decrease in the hydrogen-bonded structures.

The miscibility of polystyrene (PS)/poly(methyl methacrylate) (PMMA) and SMA/PMMA blends has been extensively investigated.[5–8] The former systems are immiscible[5] and the latter are miscible when the weight fraction of MA in SMA is in the range of 8–33 wt %.[6–8] This miscibility of SMA/PMMA blends is caused by the repulsive forces within the copolymer units, which lead to a net exothermic condition of mixing.[6] Feng et al.[7] suggested that the strong intermolecular interaction between the phenyl groups in SMA and the carbonyl groups in PMMA makes SMA/PMMA blends miscible on a molecular level.

Brannock et al.[6] reported that SMA/PMMA blends exhibit lower critical solution temperature (LCST) behavior. Their phase-separation temperature is largely dependent on the weight concentration of MA in SMA and presents a highest value of around 320°C with 14 wt % MA. However, for the same MA concentration in SMA, the phase-separation temperature is less dependent on the SMA/PMMA composition. Min and Paul[9] showed that PS/poly(vinyl

TABLE I
Characteristics of the Polymers

Polymer	M_w (g/mol)	M_n (g/mol)	Supplier
SMA	200,000	100,000	Arco Chemical Co.
PMMA	131,700	101,300	Atohaas Americas, Inc.
PVME	90,700	46,500	Scientific Polymer Products, Inc.

M_n, number-average molecular weight; M_w, weight-average molecular weight.

methyl ether) (PVME) blends are also miscible and show LCST-type phase behavior. The phase-separation temperature in these blends can be increased by the addition of comonomers to the PS phase. They showed that for SMA containing 8 wt % MA, the corresponding SMA/PVME blends presented a phase-separation temperature higher than that of PS/PVME blends by around 60°C. This was attributed to the closer solubility parameters of the styrenic copolymer and PVME. Ahn et al.[10] investigated the miscibility of SMI/styrene–acrylonitrile copolymer blends in which SMA was partially imidized by imide units of various contents and chemical structures. They showed that the type of substituent on the imide had a greater effect on the T_g values of the SMI/styrene–acrylonitrile copolymer blends than the copolymer composition.

To the best of our knowledge, no studies have previously been conducted on the effect of SMA imidization on phase-separation temperatures of SMI-based blends, and this is the objective of this work. We focus on how the miscibility and especially the phase-separation temperatures of SMA/PVME and SMA/PMMA blends are affected by SMA imidization. Moreover, differential scanning calorimetry (DSC) and small-angle light scattering (SALS) techniques have been used for phase-separation characterizations of the different blends studied.

EXPERIMENTAL

Materials

All polymers used in this study were commercial grades. Their main characteristics are summarized in Table I. SMA was supplied by Arco Chemical Corp. (Newtown Square, PA) and had 8 wt % MA. PMMA was graciously supplied by Atohaas Americas, Inc. (Philadelphia, PA). PVME was purchased from Scientific Polymer Products (Ontario, NY). 2-Amino anthracene (97%) and 1,2-dichloroethane (high-performance liquid chromatography grade) were purchased from Sigma–Aldrich, Inc. (Oakville, Canada). Aniline (analytical reagent grade) was supplied by J.T. Baker Chemical Co. (Phillipsburg, NJ). Hexane, tetrahydrofuran, and methanol solvents were guaranteed reagent grades supplied by EMD Chemicals (Gibbstown, NJ).

Synthesis of SMI

A mixture composed of 15 g of SMA and 3.3 g of aniline, which corresponded to a molar ratio of 1 : 3, was dissolved in 125 mL of xylene and stirred at 120°C in an oil bath for 22 h. The high reaction temperature and long stirring time were chosen to ensure the complete ring-closing reaction to form the imidization product. Purification of the modified polymer was achieved by precipitation in methanol followed by filtration. The solid product was then redissolved in tetrahydrofuran and reprecipitated in hexane two additional times. The purified solid sample was dried in vacuo at 70°C for 7 days and then compressed at 180°C to form a film around 200 μm thick. The imidization reaction between SMA and aniline is presented in Scheme 1.

Blend preparation

SMA (or SMI)/PVME and SMA (or SMI)/PMMA blends of various compositions were prepared as follows. The blend components were first dissolved in tetrahydrofuran or 1,2-dichloroethane as a solvent to obtain a 5% (g/100 mL) solution and then cast onto a Teflon film. The solvent was then evaporated overnight at room temperature, and the developed film was dried in vacuo at 70°C for 1 week. These evaporating conditions were chosen to ensure maximum solvent extraction from the film.

Characterization techniques

The conversion of the imidization of SMA was characterized with an attenuated total reflection (ATR) technique with a Specac FTLA 2000 instrument (ABB, Quebec, Canada) at a resolution of 4 cm^{-1} (with 16 scans). Thermogravimetric analysis (TGA) was conducted under nitrogen from 10 to 500°C at a heating rate of 10°C/min with a TGA Q500 analyzer (TA Instruments, New Castle, DE). DSC was carried out under nitrogen with a DSC Q100 system (TA Instruments) at a heating rate of 10°C/min. To ensure reproducible DSC thermograms free of a prior thermal history effect, a second scan was done, and T_g was taken from this second scan. SALS measurements were performed with a homemade setup
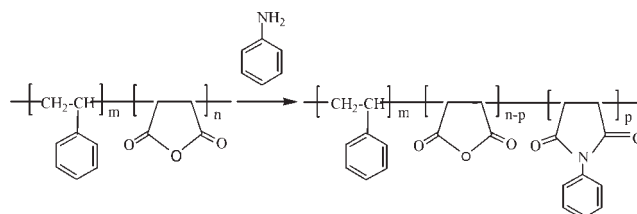
Scheme 1 Preparation of SMI by imidization between SMA and aniline.
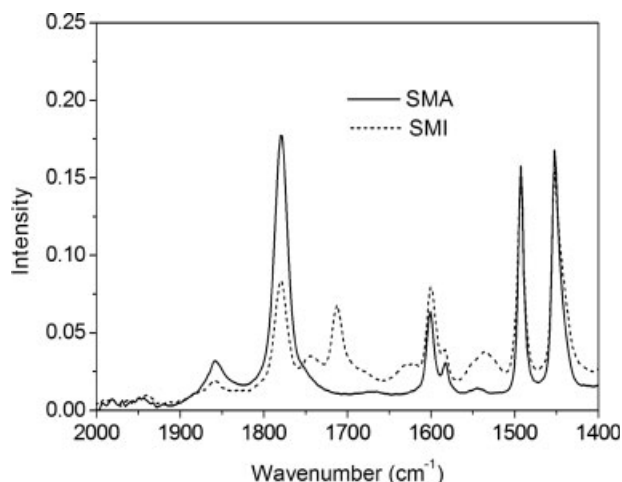
Figure 1 ATR spectra of (—) pure SMA and (- - -) the SMI copolymer.

installed on a Linkam shearing cell (Scientific Instruments Ltd., Tadworth, UK). The light source (10 mW) consisted of a He/Ne laser with a wavelength of 632.8 nm. A polarizer was placed between the light source and the sample, and a parallel analyzer was placed between the sample and a glazed PMMA screen (distance between the sample and screen = 38.7 cm). The scattering pattern of the sample was recorded with a Cooke C01300 charged coupling device camera (Cooke Corp., Romulus, MI) with a resolution of 1000 pixels × 1000 pixels at a grabbing rate of 1–10 frames/s. The recorded frames were treated with Kuleuven SALS (Katholieke Universiteit Leuven, Belgium) and Image J software. More details on the setup can be found in previous works by Deyrail et al.[11] and El-Mabrouk et al.[12] It should be mentioned that SALS characterization always requires blend samples to be annealed at temperatures around 20°C lower than their corresponding phase-separation temperatures.[12] For all SALS characterizations, SMA/PMMA and SMA/PVME films were annealed at 200 (for 2 h) and 115°C (for 60 min), respectively. Then, they were heated at a rate of 1°C/min until phase separation.

RESULTS AND DISCUSSION

ATR characterization of partially imidized SMA (SMI)

Figure 1 shows the ATR spectra of pure and imidized SMA. The peaks at 1780 and 1863 cm^{-1} on both the SMA and SMI spectra correspond to the carbonyl absorption of anhydride groups in five-membered rings. As shown on the SMI spectrum, the fact that there is no peak at 1680 cm^{-1} confirms that the amide ring is completely closed.[7] The new peaks appearing on the same spectrum at 1712 and 1602 cm^{-1} correspond to the imide group and C=C

vinyl stretching vibration of styrene, respectively. To calculate the degree of conversion of the imidization reaction with eq. (1),[13] the peak at 1602 cm^{-1} on the SMI spectrum was used because, as shown in Figure 1, this peak was not modified by the reaction:

$$P = (1 - A_t/A_0) \times 100\% \qquad (1)$$

where parameters A_0 and A_t are the ratios of the absorbance at 1780 cm^{-1} to that at 1602 cm^{-1} (taken from Fig. 1) before and after modification with aniline, respectively. According to eq. (1), the degree of conversion of the imidization reaction is 49%. The same imidization conversion could also be obtained in the transmission mode instead of ATR because the chemical structures in the bulk and at the surface are the same.

Thermal characterization of SMA and SMI

The TGA and TGA derivative curves of SMA and SMI are shown in Figure 2(a,b), respectively. The first
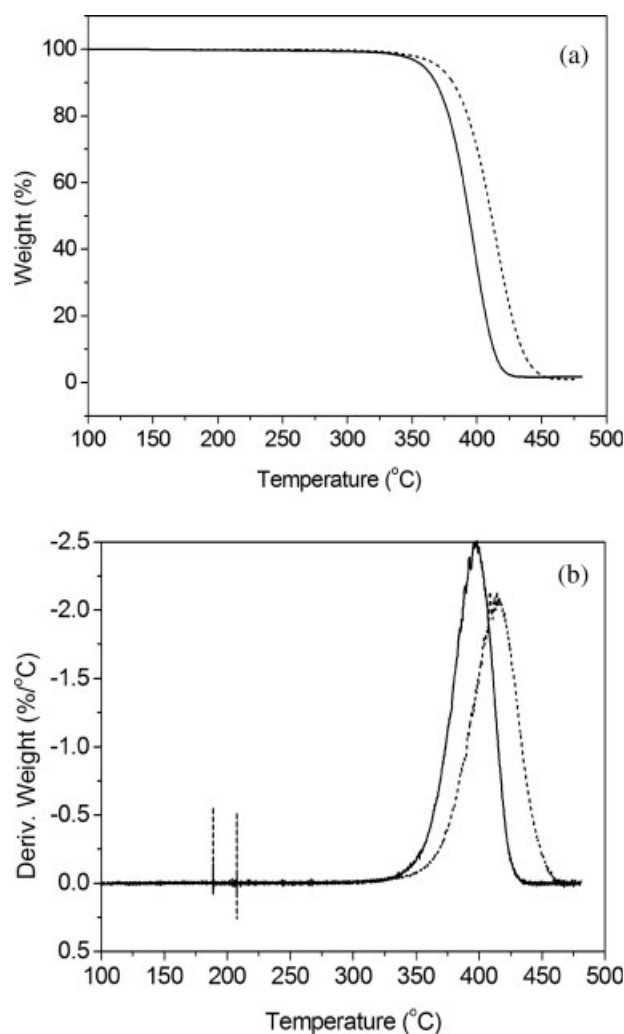
Figure 2 (a) TGA curves of (—) SMA and (- - -) SMI and (b) first-order derivatives of TGA curves of (—) SMA and (- - -) SMI.

curve gives information about the onset temperature of decomposition, which corresponds to a 5% mass fraction loss, and the second one gives the temperature at which the maximum decomposition rate occurs. The latter is also used to describe the thermal stability of the polymer. From Figure 2(a), the onset temperatures of decomposition of SMA and SMI are 358 and 370°C, respectively. This proves that the imidization of SMA improves its heat resistance. Figure 2(b) shows that SMI presents a single decomposition temperature of approximately 416°C (40% weight loss), which is higher than that of SMA (396°C; 45% weight loss). The results also show that the thermal stability of SMA is improved by imidization.
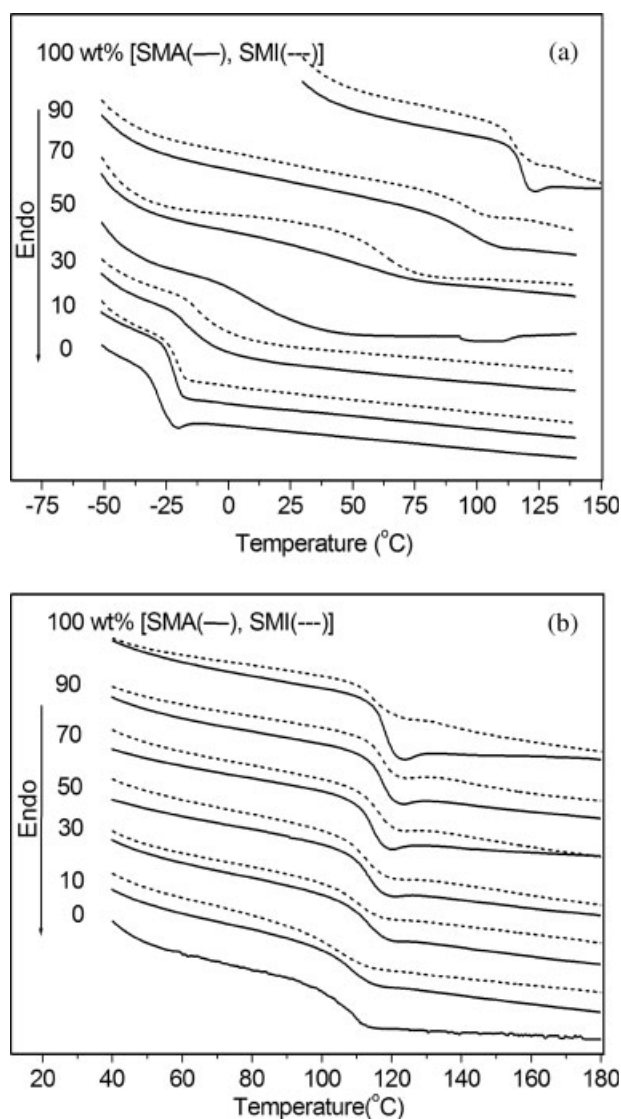
T_g characterization for SMA- and SMI-based blends

As mentioned in the Experimental section, to avoid thermal history effects, the T_g values for SMA/ (PVME or PMMA) and SMI/(PVME or PMMA) blends were taken from the DSC curves shown in Figure 3(a,b), which correspond to the second heating cycle. For all blend compositions, the figures show a single T_g value for each blend, which is a characteristic of miscible blends.

The T_g values of the different SMA- and SMI-based blends, taken from the DSC curves (with an error generally less than 1–2%), are presented in Figure 4(a,b) as a function of the SMA and SMI weight concentrations. Figure 4(a) shows that both SMA/ PVME and SMI/PVME blends show negative deviations from the additivity rule (represented by the dotted line), especially at low SMA and SMI concentrations. It also shows that T_g of pure SMI (open symbol) is slightly lower than that of pure SMA (closed symbol), as reported in the literature.[3] This small difference can be explained by the fact that the grafting of the phenyl ring reduces the packing density and consequently reduces the segmental mobility of SMI monomer units. For SMA/PMMA and SMI/PMMA blends, Figure 4(b) shows that these blends present a positive deviation from the T_g additivity rule. This proves the presence of a strong interaction between the blend components. The T_g data for both blends obey the Gordon–Taylor equation:[14]

$$T_g = (w_1 T_{g1} + K w_2 T_{g2})/(w_1 + K w_2) \qquad (2)$$

where T_{gi} and w_i ($i = 1$ or 2) represent the glass-transition temperatures and weight fractions of the blend components, respectively, and K is an optimized fitting parameter equal to 3.0 for SMA/ PMMA and 1.5 for SMI/PMMA. The lower K value for the SMI/PMMA blend means that SMI has less interaction with PMMA than SMA.

Figure 3 DSC curves for different SMA and SMI weight concentrations: (a) (—) SMA/PVME and (- - -) SMI/PVME blends and (b) (—) SMA/PMMA and (- - -) SMI/PMMA blends.

Characterization of the phase separation of SMA- and SMI-based blends by the SALS technique

A series of films made from (SMA or SMI)/(PVME or PMMA) blends with various SMA and SMI compositions were heated at 1°C/min, and the corresponding scattering patterns were recorded. In the homogeneous region, the scattering intensity is supposed to be constant, whereas after phase segregation, it increases rapidly as a function of temperature.[11,12] The point at which the scattered intensities start to increase is defined as the phase-separation temperature. Commercial SMA containing 8 wt % MA was selected for this study because it gives a low phase-separation temperature. Figure 5 shows an example of the scattering intensity as a function
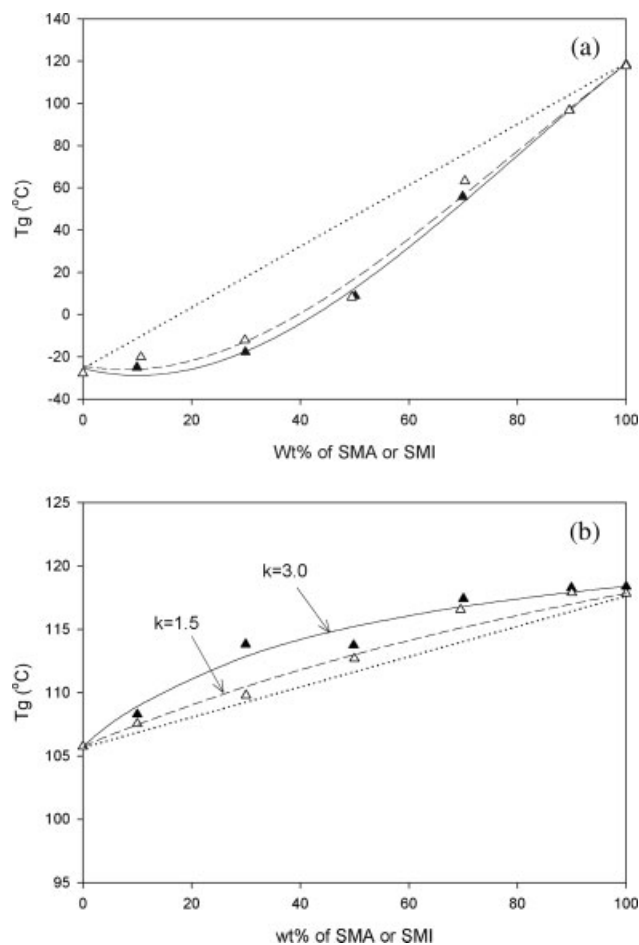
Figure 4 T_g as a function of the SMA or SMI weight fraction: (a) (▲) SMA/PVME and (△) SMI/PVME blends and (b) (▲) SMA/PMMA and (△) SMI/PMMA blends.

of temperature for an SMA/PVME blend containing 30 wt % SMA. It clearly indicates a rapid increase around 165°C, which corresponds to the phase-separation temperature of this blend.

The phase-separation temperatures taken from the scattering intensity curves of the different SMA- and SMI-based blends studied are presented in Figure 6(a,b) as a function of the SMA and SMI weight concentrations. Figure 6(a) shows that both SMA/PVME and SMI/PVME blends display LCST behavior. However, the phase-separation temperature for SMI/PVME is generally higher than that for SMA/PVME blends. The imidization reaction increases the amount of phenyl ring in SMA, which may improve the miscibility between the blend components because the electron long pairs of the PVME oxygens interact more with the π electrons of the benzene rings on SMA.[15,16] It can also be seen from Figure 4(a) that the T_g curve of SMI/PVME blends is a little higher than that of SMA/PVME. Figure 6(b) shows that for an SMA concentration less than 70 wt %, the phase-separation temperatures for SMA/PMMA blends have a low dependence on the SMA
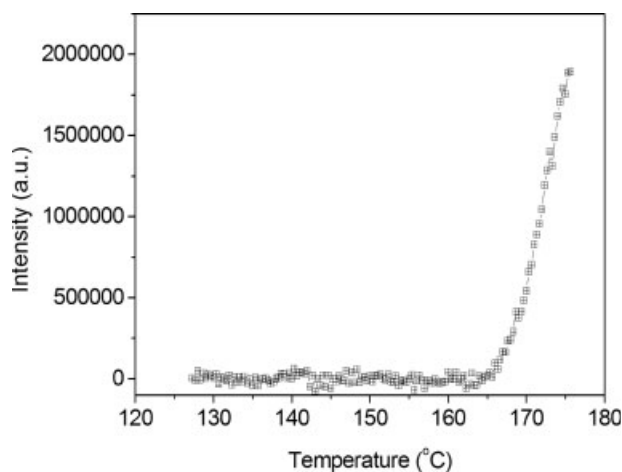
Figure 5 Scattering intensity as a function of temperature for a 30 wt %/70 wt % SMA/PVME blend.

concentration. The same behavior was also observed by Brannock et al.[6] However, SMI/PMMA blends show a convex LCST curve, and the highest phase-separation temperature was obtained at an SMI concentration of approximately 30 wt %. The miscibility
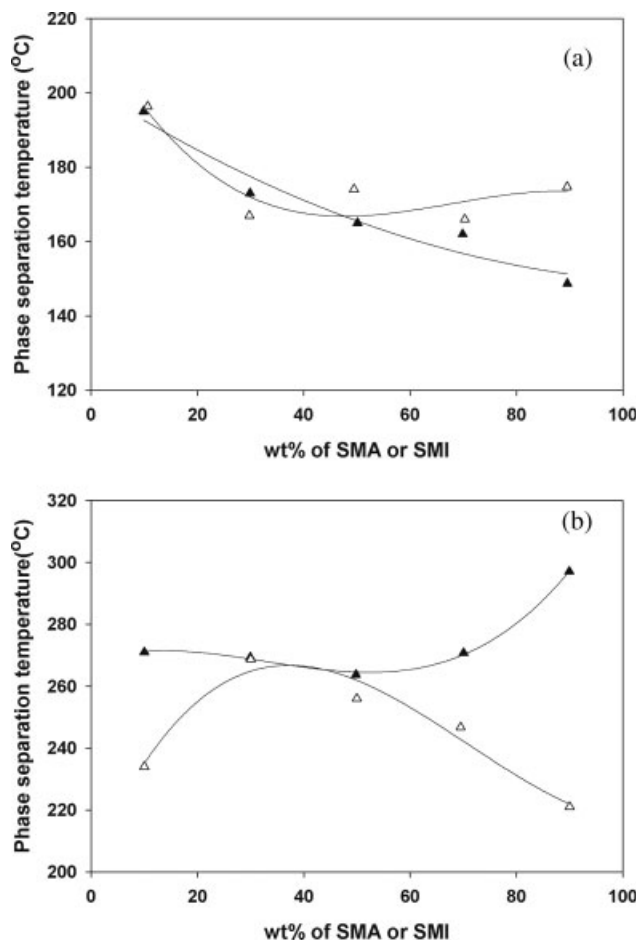
Figure 6 Phase diagrams: (a) (▲) SMA/PVME and (△) SMI/PVME blends and (b) (▲) SMA/PMMA and (△) SMI/PMMA blends.

of SMA/PMMA blends is due to the repulsive interaction between the monomer units [styrene$_{(1)}$ and MA$_{(2)}$] of the SMA copolymer.[6] The neat interaction (B) between the different components of SMA/PMMA can be related to the binary interaction parameter (B_{ij}) between the monomer units of SMA and those of PMMA [methyl methacrylate$_{(3)}$] with the following relation:[6]

$$B = B_{13}\phi_1' + B_{23}\phi_2' - B_{12}\phi_1'\phi_2' \quad (3)$$

where ϕ_1' and ϕ_2' are the volume fractions of styrene$_{(1)}$ and MA$_{(2)}$ in the SMA copolymer, respectively. Equation (3) predicts that, although all the B_{ij} values are generally positive, SMA/PMMA blends may have a window of miscibility when B is negative, that is, when the binary interaction B_{12} between styrene$_{(1)}$ and MA$_{(2)}$ in the SMA copolymer is considerably greater than their corresponding binary interactions B_{13} and B_{23} with the methyl methacrylate$_{(3)}$ monomer unit of PMMA. B_{ij} can be roughly approximated by the following relation:[17,18]

$$B_{ij} = (\delta_i - \delta_j)^2 \quad (4)$$

where δ_i and δ_j correspond to the solubility parameters of the pure blend components i and j. These are given by the following relation:[18]

$$\delta = \sqrt{\Delta E / V} \quad (5)$$

where ΔE is the energy of vaporization of the pure component and V is its molar volume. The solubility parameters for PS, poly(maleic anhydride), and poly(*N*-phenyl succinimide), calculated according to eq. (5), are 9.1, 13.7, and 11.4 cal$^{1/2}$/cm$^{3/2}$, respectively. With these values in eq. (4), the binary interaction between the styrene and MA monomer units of SMA (21.2 cal/cm^3) is much higher than that between the styrene and *N*-phenyl succinimide monomer units of SMI (5.3 cal/cm^3). Therefore, the grafting of SMA with the phenyl ring reduces the repulsive interaction between the monomer units of SMA, leading to lower B values of the SMI/PMMA blends, as already mentioned in the last section. Therefore, the phase-separation temperatures of SMI/PMMA blends are lower than those of SMA/PMMA blends.

CONCLUSIONS

In this work, the thermal stability of SMA was improved by partial imidization with aniline, which led to an SMI copolymer. ATR characterization showed that the degree of conversion of the imidization reaction was 49%, and TGA showed that the thermal stability of SMA was improved by imidization; its decomposition temperature was improved by about 20°C.

The miscibility and phase-separation temperature of SMA/(PVME or PMMA) and SMI/(PVME or PMMA) blends with various SMA and SMI compositions were investigated with DSC and SALS techniques, respectively. DSC characterization showed that SMA/PVME and SMI/PVME blends presented negative deviations from the T_g additivity rule, and because of the segmental mobility reduction of SMI monomer units, T_g of pure SMI was slightly higher than that of pure SMA. On the contrary, SMA/PMMA and SMI/PMMA blends presented a positive deviation from the T_g additivity rule because of the strong interaction between the blend components. It was shown for these blends that SMI had less interaction with PMMA than SMA. SALS characterization of SMA/PVME and SMA/PMMA blends led to the following conclusions. First, the imidization of SMA caused an increase in the SMA/PVME phase-separation temperature. This increase was attributed to the increased intermolecular interaction between electron long pairs of the PVME oxygens and the π electrons of the benzene rings on SMA. Second, for the SMA/PMMA blend, the imidization of SMA led to convex LCST behavior and decreased the blend phase-separation temperature by decreasing the repulsive effect between the monomer units of SMA.

References

1. Syed, A. U.S. Pat. 6,858,672 (2005).
2. Bayram Zengin, H.; Boztuğ, A.; Basan, S. J Appl Polym Sci 2006, 101, 2250.
3. Vermeeschm, I.; Groeninckx, G. J Appl Polym Sci 1994, 53, 1365.
4. Liu, H. Y.; Cao, K.; Yao, Z.; Li, B. G.; Hu, G. H. J Appl Polym Sci 2007, 104, 2418.
5. Chuai, C.; Almdal, K.; Jyngaae-Jørgensen, J. J Appl Polym Sci 2004, 91, 609.
6. Brannock, G. R.; Barlow, J. W.; Paul, D. R. J Polym Sci Part B: Polym Phys 1991, 29, 413.
7. Feng, H. Q.; Shen, L. F.; Feng, Z. L. Eur Polym J 1995, 31, 243.
8. Fang, H. X.; Mighri, F.; Abdellah, A. J Appl Polym Sci 2007, 105, 2955.
9. Min, K. E.; Paul, D. R. J Polym Sci Part B: Polym Phys 1988, 26, 2257.
10. Ahn, T. O.; Lee, S. S.; Park, L. S.; Jeong, H. M. Polymer 1995, 36, 4347.
11. Deyrail, Y.; El Mesri, Z. E.; Huneault, M.; Zeghloul, A.; Bousmina, M. J Rheol 2007, 51, 781.
12. El-Mabrouk, K.; Belaiche, M.; Bousmina, M. J Colloid Interface Sci 2007, 306, 354.
13. Lee, S. S.; Ahn, T. O. J Appl Polym Sci 1999, 71, 1187.
14. Gordon, M.; Taylor, J. S. J Appl Chem 1952, 2, 493.
15. Tran-Cong, Q.; Kawakubo, R.; Sakurai, S. Polymer 1994, 35, 1236.
16. Tran-Cong, Q.; Nakano, H.; Okinaka, J.; Kawakubo, R. Polymer 1994, 35, 1242.
17. Zhu, S.; Paul, D. R. Polymer 2003, 44, 5671.
18. Coleman, M. M.; Serman, C. J.; Bhagwagar, D. E.; Painter, P. C. Polymer 1990, 31, 1187.